Narrative Progress Report for Shantz ACS PRF ND award 57697-ND5

1. PRF# 57697-ND5
2. Project Title: Cerium Oxide Clusters and Particles as Catalysts for the Oxidation of Benzene to Phenol
3. PI: Daniel Shantz, Tulane University
4. No Co-PI

Research Impact:

This project has had three major thrusts over the current reporting cycle. The first was finishing up the work that was the last thrust in the 2018 report, using Fe-MFI to convert benzene to phenol. The key points are shown below: (Fig.1):

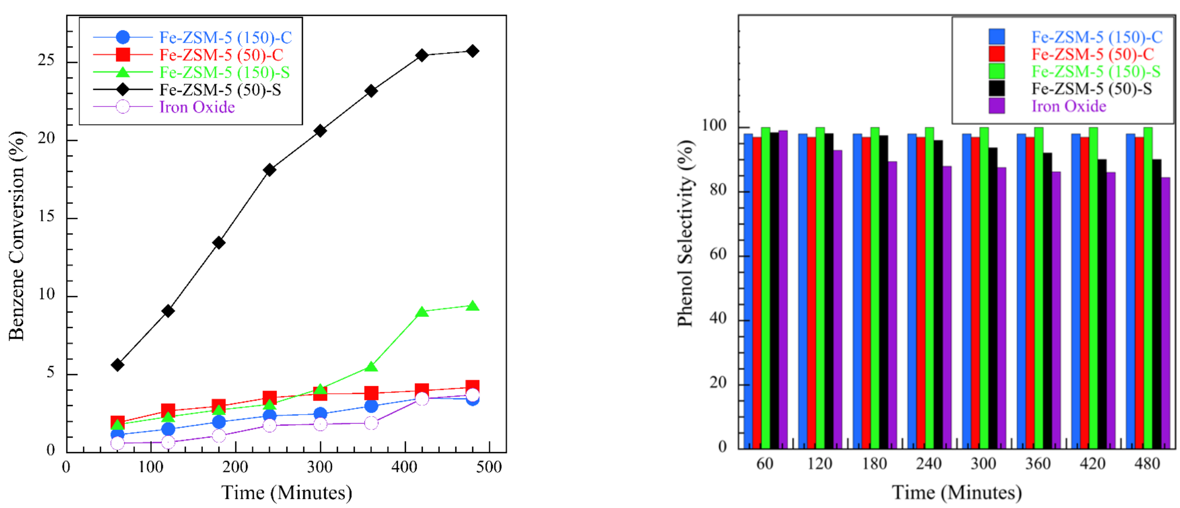

Figure 1. Benzene conversion/phenol selectivity versus time over calcined Fe-ZSM-5 samples and α-Fe_2O_3 particles at 333 K

This work was published in *The Journal of Catalysis* in late 2018. The second thrust was exploring the samples above for the direct oxidation of methane to methanol/formic acid using hydrogen peroxide as an oxidant. That unfortunately did not work; however, we investigated other Fe-MFI variants and in fact we found that it was possible to make catalysts that were active for the oxidation of benzene to phenol. A few key points emerged from our work:

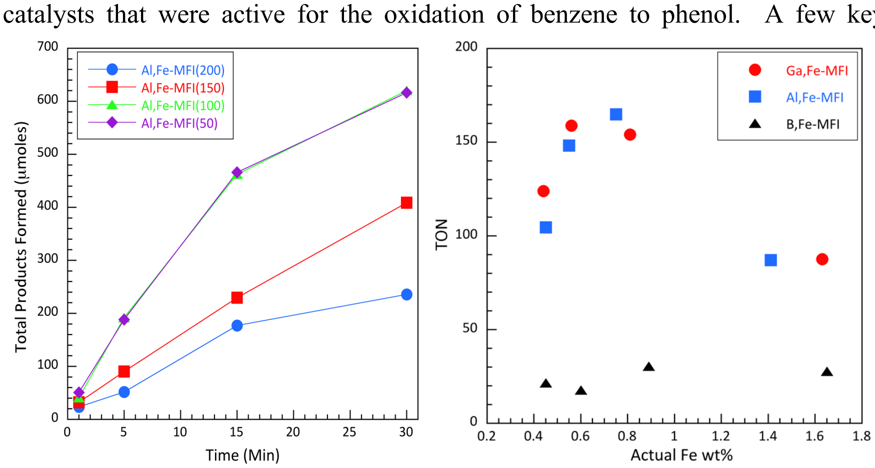

Figure 2. Typical production rate profile (left) for Al,Fe-MFI as a function of iron content, and (right) turnover number for the various zeolite samples investigated.

1. In contrast with work from the Hutching lab we found that we could make zeolites with iron contents up to nearly 1 wt% that remained active and selective for the direct oxidation of methane to formic acid

2. The presence of Bronsted acid sites were key for this reaction, and clear correlation was observed with both 1) the iron content and 2) the presence of strong acid sites.

This was has recently appeared in *Catalysis Science and Technology*. The third thrust has been the partial oxidation of methane to methanol using molecular O_2 as an oxidant. The most interesting finding to date is that mixed beds of Cu-SSZ-13 and H-SSZ-13 lead to a substantive (30%) increase in the site time yield of methanol.

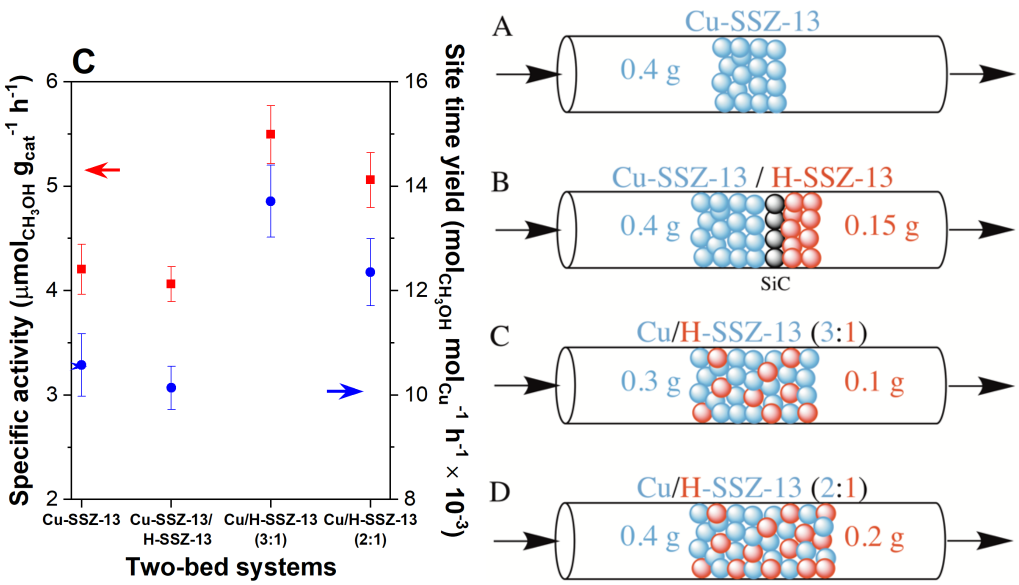

Figure 3. (Left) Specific activity (red) and site time yield (blue) in methane partial oxidation to methanol and (right) bed configuration for the catalysts used. A) 0.4 g of Cu-SSZ-13 was used for the standard reaction. B) 0.4 g of Cu-SSZ-13 was packed in the reactor with 0.15 g of H-SSZ-13 and physically separated by SiC chips. The sample was labelled as Cu-SSZ-13/H-SSZ-13. C) 0.3 g of Cu-SSZ-13 was mixed with 0.1 g of H-SSZ-13 and labelled as Cu/H-SSZ-13 (3:1). D) 0.4 g of Cu-SSZ-13 was mixed with 0.2 g of H-SSZ-13 and labelled as Cu/H-SSZ-13 (2:1).

Impact on the PI's Career

The main impact this work (and support) has had on the PI is to allow him to initiate work in the oxidation catalysis space. The best catalysts discovered so far are very encouraging. The PI plans to leverage this work to further his efforts in the oxidation catalysis space to explore the direct oxidation of methane to methanol, a topic of great interest in the U.S. due to the abundance of shale gas. The additional student year that the reorganization of the budget allowed was key to this and is the reason the PI was able to work on the methane to methanol work above (thrust three).

Impact on the students supported

The students involved in this work will obtain high visibility due to the importance of the problem and the nature of the journal in which the work will be published. Both students who have been supported on this award during the current cycle are interested in academic careers, and this program should align them well with that aim. As one example, INE.OS has contacted me about our work given their interest in phenol production technology